LIGHT ABSORPTION IN PARAMAGNETIC IONS IN STATE OF SOLUTION. PART III. Cr^{+++} ION

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ABSTRACT. Light absorption in Cr^{+++} ion salts is studied by a 'Hilger's "UVISPEK" spectrophotometer in the range 3900 Å to 10,000 Å and the results are discussed in the light of crystalline electric field theory.

It is observed that the overall cubic splitting is much larger in Cr^{+++} salts compared to Cu^{++}, Ni^{++} and Co^{++} ion salts. The co-valency factor f^2 as deduced from the lowering of the term separation arises from σ-and π-orbital overlap in Cr^{+++} ion salts.

The average magnetic moment and g-values evaluated with the help of the optical data agree very well with those observed experimentally.

The effect of the long range fields on the water cluster was found to depend on the value of f^2, since this is dependent on stabilizing energy, which is measured by f^2-values. It was observed that this effect was most pronounced in Co^{++} ion (f^2 0.95) and the least pronounced in Cr^{+++} ion (f^2 0.75).

INTRODUCTION

In the second part of this paper (Mookherji and Chhonkar, 1960), which we shall refer as Part II hereafter, a systematic optical investigation of the consequences of the crystalline electric field on the optical and magnetic behaviour of Ni^{++} ion in about twenty salts in aqueous solution has been reported. A number of interesting results that have been obtained are:

a) The energy of separation of the mean centre of the absorption bands is almost wholly determined by the cubic part of the crystal field and that the anisotropic part has little influence on this.

b) There is weak covalent bonding in Ni^{++} ion arising from the partial overlap with σ- and π-orbitals of the surrounding atoms, which lowers the term separation from the free ion value. π- orbital overlap is negligible in the ordinary salts of Ni^{++} ion.

c) The measured finer splitting of the bands due to the tetragonal part of the field gave excellent agreement with the magnetic anisotropy values obtained from the susceptibility measurements.

d) The contribution of the distant atoms to the anisotropy of the water cluster about the Ni^{++} ion was found to be pronounced in certain salts; while in others they were not so pronounced.

The ground state of the free Cr^{+++} ion is an F-state ($3d^3$ ^4F) like Ni^{++} ion ($3d^{8}{}^3F$) but with a spin moment 3/2 instead of 1 as in Ni^{++} ion. Just like octahedrally coordinated Ni^{++} ions Γ_2 orbital singlet level lies lowest in the Stark pattern for Cr^{+++} ion with similar coordination. But two facts, that the spin-orbit coupling in Cr^{+++} ion is $+87$ cm^{-1} (Laporte, 1928) as against -328 cm^{-1} in Ni^{++} ion and that Cr^{+++} ion with 3 electrons as against 8 in Ni^{++} ion has Kramers spin degeneracy, make the situation for Cr^{+++} ion somewhat different. Moreover, due to larger charge on Cr^{+++} ion the electrons of oxygens of the water cluster about Cr^{+++} ion will have a greater tendency to move into the central ion orbitals in order to stabilize its potential energy and hence both σ- and π-orbital overlap may be present in Cr^{+++} ions (Owen, 1955). This stabilization may tend to reduce the secondary distortions of the octahedral cluster and hence the splitting by the tetragonal part of the field will be very small. The small positive value of λ together with the small tetragonal splitting will make the magnetic anisotropy for Cr^{+++} ion much smaller compared to the anisotropy of the Ni^{++} ion and the magnetic moment will tend to have almost the spin-only value. Moreover, spin-orbit contribution from the upper cubic levels will be smaller compared to Ni^{++} ions and hence the effect of the distant atoms may be expected to be less pronounced in Cr^{+++} ion salts. It is, however, to be remembered that owing to the lowest state in Stark pattern being an orbital singlet, Jahn-Teller distortion should be almost absent and practically the entire anisotropy should arise from the induced distortion of the octahedron by the effect of the long range atoms.

It would, therefore, be interesting to study the optical absorption spectra of a number of chromic salts and view them in the light of the findings of magnetic susceptibility and other measurements.

EXPERIMENTAL

The measurements were carried out by Hilger's "UVISPEK" spectrophotometer and the same procedure as in Part I of this paper (Mookherji and Chhonkar, 1959) was adopted. The chemicals used were of 'Merck's gravimetric reagent quality Triple distilled water was used for making solutions.

The measurements were centred round 27°C, but no observable change in the position of the absorption bands was noted for small room temperature variations.

RESULTS

The results of measurements are collected in Table I. The locations of the absorption bands for various salts of solution are given both in wavelengths and

in wave numbers. In order to get prominent absorption peaks for the salts studied we had to use dilute solutions. Progressive dilution from that concentration at which prominent absorption peaks are obtained does not change the positions of the absorption peaks.

TABLE I

Salts	Concentrations %	Maximum absorption			
		Wave length in Å		Wave numbers (cm^{-1})	
		I	II	I	II
$Cr_2(SO_4)_3$	0.5	5880	4225	17,010	23,670
$Cr_2(SO_4)_3.K_2SO_4$	1.0	5790	4095	17,270	24,420
$CrCl_3$	1.0	5810	4115	17,210	24,300
$Cr(NO_3)_3$	1.0	5775	4085	17,310	24,480
$Cr(C_2H_3O_2)_3$	0.3	5670	4110	17,640	24,330

The variation of absorption in different salt solutions are shown graphically in Figs. 1 to 2.

DISCUSSION

a) *The absorption spectra*

In all the five chromic salts studied by us the absorption spectra consist of two maxima, one at about 17,300 cm^{-1} and the other at about 24,300 cm^{-1}. We shall designate them as I and II respectively. The maximum which lies in the ultra violet region near 38,000 cm^{-1} (Owen, 1955) will be known as III.

The spin-orbit coupling constant $\lambda = +87$ cm^{-1} is only one fourth of that of nickel salts and hence the splitting due to the tetragonal field will be very small compared to the Ni^{++} ion. This is also what is observed experimentally (Krishnan, Mookherji and Bose, 1939) and hence optically we should expect only three main transitions, two being in the visible region and the other one in the ultra violet region.

The maxima I and II may be identified as arising due to the transitions between the Stark levels ($\Gamma_2 - \Gamma_5$) and ($\Gamma_2 - \Gamma_4$) respectively. In our later discussions these transitions will be represented as ΔE_b and ΔE_c respectively (Fig. 3).

b) *Crystal field and energy levels*

The ground state of free Cr^{+++} ion is $3d^3\ {}^4F$ and the term of the same multiplicity (^4P) lies 13,770 cm^{-1} above it (Moore, 1952). The type of the complex ions that we shall be dealing in this paper has the Cr^{+++} ion at the centre of a

compressed octahedron of water molecules i.e. four dipoles μ at $(\pm a, 0, 0)$ and $(0, \pm a, 0)$ and two dipoles μ' at $(0, 0, +b)$. Then the electric field potential at (x, y, z) near the Cr^{+++} ion at (0, 0, 0) is of the form as given by Eq. (1) of Part II.

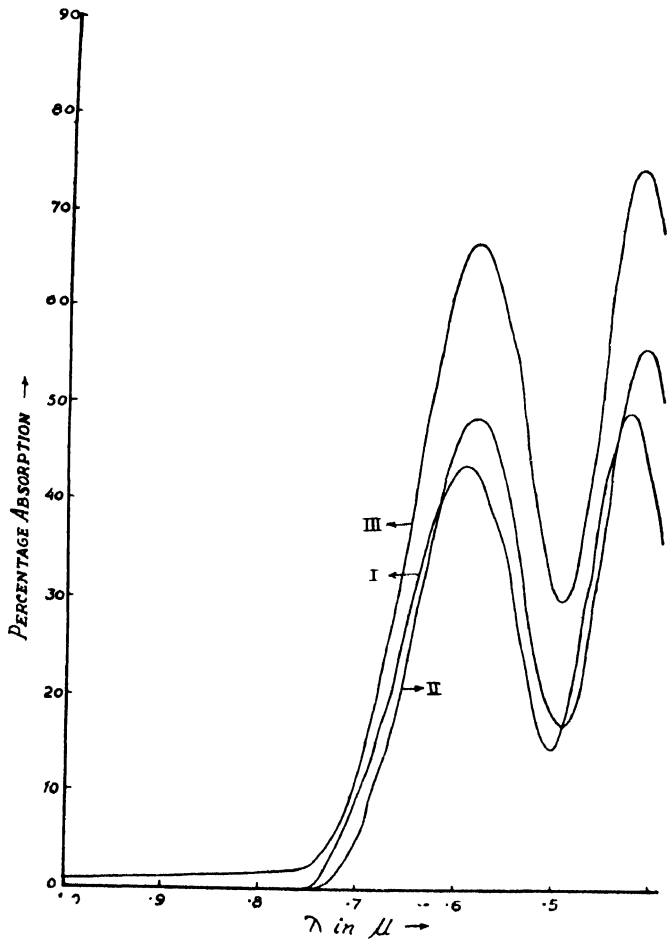

Fig. 1. Absorption curves (aqueous solution) of
(I) 0.5% $Cr_2(SO_4)_3$
(II) 1.0% $Cr_2(SO_4)_3.K_2SO_4$
(III) 1.0% $CrCl_3$

The crystal field conforming to a potential as given by Eq.(1) of Part II splits the ground state ^4F into a number of levels whose approximate energies, according to Owen (1955) are shown in Fig. 3 and also given by Eq. (2) of Part II.

The measured magnetic anisotropy for Cr^{+++} ion in crystals is very small (Krishnan *et al.*, 1939), and tetragonal separation in state of solution will be

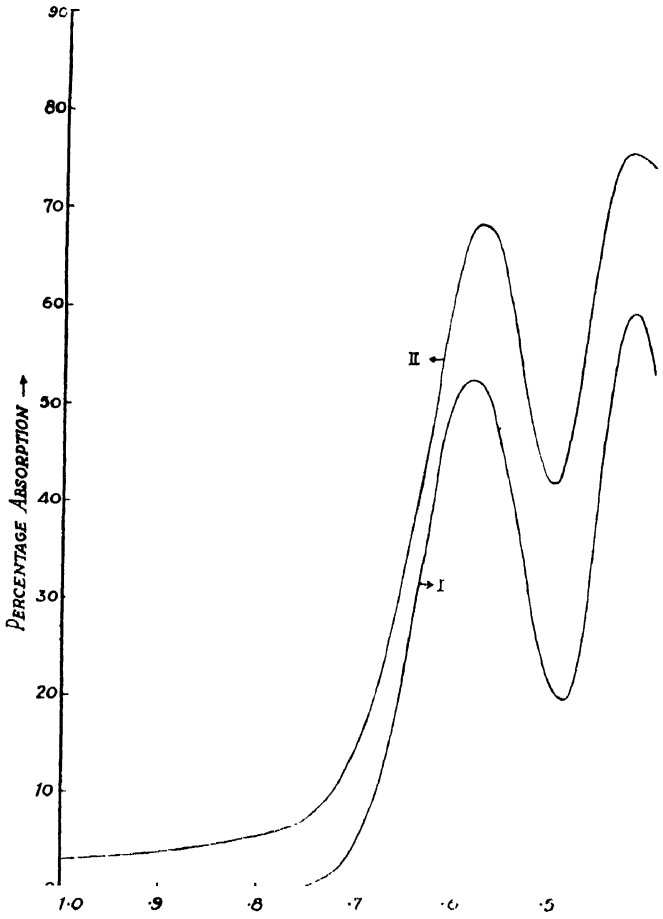

Fig. 2. Absorption curves (aqueous solution) of
(I) 1.0% $Cr(NO_3)_3$
(II) 0.3% $Cr(C_2H_3O_2)_3$

correspondingly less and hence neglecting T_4 and T_2 terms in Eq. (2) of Part II we have

$$\frac{6}{7}K - X = \Delta E_c$$

and

$$\frac{10}{21}K = \Delta E_b$$

We have observed both ΔE_c and ΔE_b experimentally (Table I) and hence K and X can be approximately evaluated. These are given in Table II.

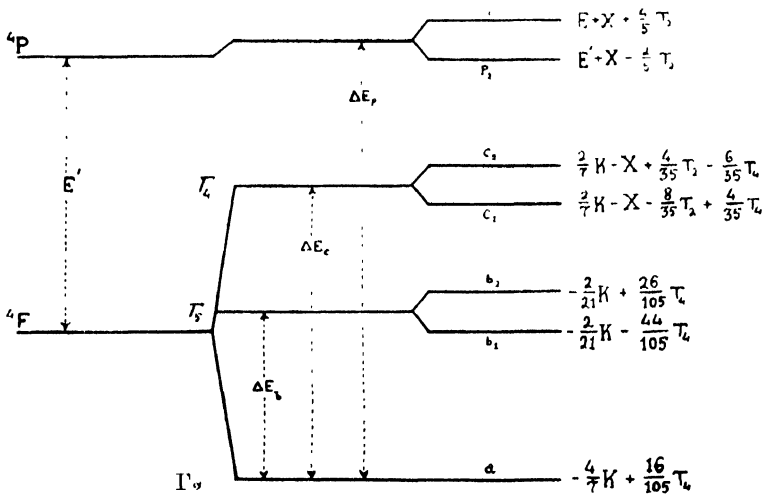

Fig. 3 Stark splitting of the ground state of Cr^{+++} ion.

TABLE II

Salts	K cm⁻¹	X cm⁻¹	E′ cm⁻¹	f2
$Cr_2(SO_4)_3$	35,720	6950	9870	0.717
$Cr_2(SO_4)_3.K_2SO_4$	36,267	6666	10950	0.795
$CrCl_3$	36,140	6680	10650	0.773
$Cr(NO_3)_3$	36,350	6680	10030	0.730
$Cr(C_2H_3O_2)_3$	37,045	7420	9810	0.712

These K-values indicate that in state of solution all the six members of the cluster about the Cr^{+++} ion may be the same in all the salts except the last in Table II studied by us.

It would be interesting to compare the magnitudes of K-values of Cu^{++} and Ni^{++} ions with those of Cr^{+++} ion. We find that in ordinary ionic salts of Cu^{++} ion (Part I, 1959) and of Ni^{++} ion (Part II) the magnitudes of K are about 25,000 cm^{-1} and 17,700 cm^{-1} respectively, while in ordinary chromic salts its value is approximately 36,300 cm^{-1}. Hence the overall separations (10/21 K) in Cu^{++} ion and (6/7K) in Ni^{++} ion and Cr^{+++} ion are 12,400 cm^{-1}, 15,200 cm^{-1} and 24,400 cm^{-1} respectively and hence it is highest in Cr^{+++} ion salts.

c) *Evaluation of the term separation* (E')

For Cr^{+++} ion where ^4F-term lies lowest, the term separation E' in crystals which is an important spectroscopic constant, can be evaluated from the expression (1) as given below (Owen, 1955):

$$X = -\left(\frac{E'+\frac{2}{7}K}{2}\right)+\left[\left(\frac{E'+\frac{2}{7}K}{2}\right)^2+K^2\right]^{\frac{1}{2}} \qquad (1)$$

where symbols have their usual meanings.

Now utilising our calculated K- and X-values (Table II) we have evaluated E'-values from Eq. (1). These are given in Table II. It is seen that there is a lowering of the term separation for Cr^{+++} ions in crystals from the free ion value $E = 13{,}770\ cm^{-1}$. Following Owen (1955) this lowering may be attributed to the covalency factor f^2, where $f^2 = f_\sigma^2 . f_\pi^2$, arising from partial overlap of the 3d-orbitals with σ- and π-orbitals of the surrounding atoms. Accordingly,

$$\frac{E'}{E} = f^2 \qquad \ldots \quad (2)$$

From Eq. (2) one can calculate f^2 which are given in Table II.

Primarily this covalency factor should not be different for all the salts in which Cr^{+++} ion is similarly coordinated with six water molecules, but there might be an appreciable change in the overlap between Cr^{+++} ion and oxygen and hence in the covalency factor from salt to salt arising from the effect of distant atoms. In state of solution distant atom effect will be negligible and hence covalency factor should not vary appreciably from salt to salt with similar coordination. Bose and Mitra (1952) in their masterly survey of the comparative influence of short and long range fields on the magnetic behaviour of salts of iron group of elements came to the conclusion that long range field effect in Cr^{+++} ion salts will be less pronounced than Ni^{++} ion salts.

It is seen that these f^2-values are considerably smaller than those of Cu^{++} (0.85) and Ni^{++} (0.9) ions. This demands a stronger bonding in Cr^{+++} ion, which is to be attributed to the larger charge on it. As a result of this larger charge the electrons on the oxygen have got a tendency to move into the central chromic ion in order to even out the charge distribution. Under such state of affairs we are no longer justified to take π-bonding as weak and hence f^2 in them will consist of both f_σ^2 and f_π^2. Moreover, if σ-bonding is strong there may be some amount of π-bonding which will decrease the hyperfine structure in hydrated complexes of Cr^{+++} ions as actually observed by Bowers (1952) and Baker and Bleaney (1952).

From the above discussion it seems that in $[Cr(H_2O)_6]^{+++}$ complexes f_π^2 will tend to a value ~ 0.9 and f_σ^2 to a value ~ 0.85, making $f^2 = f_\sigma^2 . f_\pi^2 = 0.76$ as actually observed (Table II).

d) *Calculation of magnetic moment values* :

The expression for the mean magnetic moment for Cr^{+++} ion will be almost similar to that for Ni^{++} ion excepting that the spin-only value will be 15 instead of 8, and will be given by the Eq. (9) of Part II and hence the mean magnetic moment is given by

$$\mu^2 = 15[1+(8\lambda - 3kT).\alpha'] \qquad \ldots \quad (3)$$

where $$\alpha' = f^2 . \alpha = -\frac{f^2}{\Delta E_b} = -2.1\frac{f^2}{K}$$

It is interesting to note that the last two terms in the expression (3) which represent the deviation of the effective magnetic moment from its spin-only value are of opposite sign. The comparative strengths of the two terms at 300°K will be

$$8\lambda = 696 \text{ cm}^{-1}$$

and $$3kT = 630 \text{ cm}^{-1}$$

The difference in them is only 66 cm^{-1} which when multiplied by α' having a negative value will bring down the spin-only value by about 0.004. Hence the relative contribution from these two terms is very very small as is shown below :

$$\mu^2 = 15(1 - 0.04 + 0.037)$$

It is therefore clear that in chromium salts there will be very small deviation ($\approx 0.4\%$) from the spin-only value.

Now utilising our calculated values of K, f^2 and the Eq. (3) we have evaluated μ-values for Cr^{+++} ion in state of solution for different salts. These are given in Table III. For comparison we have included solution values in the Table. It is seen that the two values (optical and magnetic) agree well within the experimental errors.

These values of the mean magnetic moment for Cr^{+++} ion salts have almost the spin-only value (3.87) as has already been shown above.

TABLE III

Salts	μ-Values		g-Values	
	Optical (soln.)	Magnetic (soln.)	Optical	Crystal
$Cr_2(SO_4)_3$	3.867	3.850*2	1.970	1.980*
$Cr_2(SO_4)_3.K_2SO_4$	3.866	3.778*3	1.968	1.980*
$CrCl_3$	3.867	3.850*2	1.989	1.990**
$Cr(NO_3)_3$	3.867	3.745*4	1.968	2.260***
$Cr(C_2H_3O_2)_3$	3.868	3.756*1	1.972	———

*Ting and Williams, 1951.

**Kozyrev, Salikhov and Shamonin, 1952.

***Lancaster and Gordy, 1951.

*1 Mookherji, T. (Unpublished)

*2 Cabrera, Marquina, 1922.
*3 Welo, 1929.
*4 Fahlenbrach, 1932.

For complete reference consult Selwood's, Magnetochemistry.

e) *Calculation of g-values* :

The spectroscopic splitting factor g for Cr^{+++} ion according to Owen (1955) is given by

$$g = 2 - \frac{12\lambda}{\Delta E_b} f^2 = 2 - \frac{25.2\lambda}{K} f^2 \qquad \ldots \quad (4)$$

Substituting the values of K and f^2 from Table II, g-values could be calculated which are given in Table III. In the absence of any experimental g-values in state of solution for Cr^{+++} ion we have included crystal g-values in the table for comparison. It is seen that g-values in state of solution and in crystal do not vary appreciably.

From our optical measurements we observe that f^2-values in Cr^{+++}, Cu^{++}, Ni^{++} and Co^{++} ions are ~0.75, ~0.85, ~0.9 and ~0.95 respectively (Mookherji and Chhonkar, 1959, 1960). f^2-Values give the covalent character of the ions; so the covalent character will go on decreasing as we go from Cr^{+++} to Co^{++} ions. Further, more covalent the ion is, the more stable will be the water cluster surrounding it. As a result, the stabilizing energy in case of Cr^{+++} ion will be larger compared to others and that this will tend to minimise the secondary distortions of the octahedral cluster. We have already seen that these secondary distortions will be produced by the effect of the distant atoms alone and that too will be minimised by the high stability of the water cluster. That this effect is very small is also supported by magnetic anisotropy measurements (Krishnan *et al*, 1939). It is therefore, clear from the above discussion that the distant atom effect in Cr^{+++} ion will not be pronounced: whereas this should be most pronounced in Co^{++} ion, less in Ni^{++} and almost negligible in Cu^{++} ions.

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